Mineralogical Study of Silica From Opaline Levels (Salamanca, Spain) by Scanning Electron Microscope With Energy Dispersive X-RAY Attachment.

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cuadernos. laboratorio xeolóxico de laxe, nº 2, 1981

ABSTRACT

Several samples, from continental sediments on granites, schists and sandstones, had been studied with the help of a SEM. After this work, different types of morphology of opaline silica are observed. The opal-CT crystal blades intergrow, given rise to spherical aggregates or «lepispheres», which appear into cavities in massive opals; this is favored (quantity, development, etc.) when the fluid medium was relatively pure, with few ions of other elements. The presence of other cations in more open spaces leads to crystaline groupings of layers, in some events alternating with iron minerals.

The origin of these formations is an exogenetic process, by evaporation of supersaturated solutions, rich in silica, wich had led to the deposit of siliceous polymorphs, whose recrystalization and increasing ordering involves an increase in density and important changes in volume.

RESUMEN

Las muestras estudiadas corresponden a sedimentos continentales que aparecen sobre granitos, esquistos o areniscas. Con ayuda del microscopio electrónico de barrido, dotado de accesorios para el análisis puntual, se han encontrado diversas morfologías de polimorfos de sílice de baja temperatura: formas hojosas o laminares, esferas constituídas por individuos planos, etc. Las lepisferas se encuentran en huecos de la masa opalina, allí donde las disoluciones residuales han sido relativamente puras; en otro caso, se depositan otros minerales sobre esta capa de ópalo-CT (cristobalita-tridimita de baja temperatura). La presencia de otros cationes o aniones causa una modificación de la superficie reactiva de la sílice, con la posibilidad de génesis de otras especies minerales.

Estas masas opalinas se han originado en un proceso de meteorización relicta, por evaporación de aguas cargadas de sílice, procedente de la descomposición meteórica de las rocas del basamento. Durante el proceso de diagénesis hay una ordenación creciente, lo que implica cambios importantes de volumen y densidad, que se traducen en reajustes posteriores en la mineralogía.

INTRODUCTION

The discovery of disorganized silica polymorphs which cement continental detritic sediments (sand and conglomerates) in the province of Salamanca is very recent (SANCHEZ CAMAZANO and SAAVEDRA, 1979) in spite of the fact that they are present in the capital of the province itself. These levels, whose age has as yet not been well established (Prelutetien) are

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also extended into various areas of neighbouring provinces. SANCHEZ CAMAZANO and SAAVEDRA (op. cit.) describe several outcrops and indicate the mineralogical composition. As well as opal-A (JONES et al., 1971), opal-CT may be found. Quartz, kaolinite, iron oxides, are frequent but no constant. At times, alunite is extremely abundant. Montmorillonite does not appear.

A genetic mechanism for these materials has been proposed by SAAVEDRA and SANCHEZ CAMAZANO (in press). These authors underline the evolved nature of the detritic grains (angular and rounded quartzs), the presence of fragments of opaline material itself, the filling of a paleorelief and the association to shield zones in which the relict meteorization evidences a loss of silica in an arid or semi-arid climate. The evaporation of silica-bearing water, during the dry period, originated from the aforesaid meteorization, together with the contribution of more acidic percolating solutions, leads to the deposition of opal.

The work described in this paper involves the use of the technique of scanning electron microscopy for the study of the siliceous materials of the above mentioned meteorization; the mineralogy has been checked by dispersive energy of X-ray.

PREPARATION OF SAMPLES

Inmediately after fracturing, the samples were mounted on aluminium stubs and coated with an evaporate gold film, before examination with a scanning electron microscope Phillips 500 model at 25 kv. Al figures are scanning electron micrographs.

DESCRIPTION

For the purposes of this study, 14 samples of opal which cemented and filled cracks were selected with different external characteristics (colour, beded or massive structure, etc.). They correspond to three different areas: in the first, the area inmediately around the city of Salamanca, it appears in sand and very mature conglomerates. In the second, Aldearodrígo, in granite which was initially meteorized and then compacted, and in the deepest zones of a lateritic type of meteorization. In all the localities, similar phenomena are observable with very variable amounts of opal.

The mineralogical composition corresponds to that showed by SANCHEZ CAMAZANO and SAAVEDRA (op. cit.). The opal with massive shape seems to invade some previous minerals (fig. 1) and to set in others (fig. 2). Different types of morphology of opal-CT is founded; laminar aggregates give an aspect of compact nodules on large surfaces (figs. 3, 4 and 5). According to our news these forms were not described by others workers. The opal-CT platelets, with serrated edges, which are either subparallel (fig. 6), or penetrating each other, appear in layer alternating with other constitued for Fe minerals (figs. 7 and 8) or coating the interior of walls of open cavities (fig. 9).

Finally, spherical aggregates forms, «lepispheres» (WISE et al., 1972), and coalescent lepispheres appear in holes (figs. 10, 11, 12, and 13). The gradual development of these structure, from isolated blades to lepispheres and coalescente aggregates, have described (FLORKE et al., 1976).

On these opal-CT shapes, some minerals are developed, figs. 14 (detail of fig. 11) and 15, which will be matter of a posterior publication.

Similar forms to these have been reported in world literature in the study of opals of varying origin, above all in marine sediments (SEGNIT et al., 1970, 1973; POLLARD et al., 1973; MURATA et al., 1975; FLORKE et al., 1975, and many more). The descriptive studies have shown that the morphology of opal-CT varies with the conditions of crystalization.

GENESIS

The hypothesis of SAAVEDRA and SANCHEZ CAMAZANO (op. cit.) for the origin of opal is based on an evaporation and, at times, mixture of siliceous waters with other, more acidic and superficial, both generated in the same meteorización process. Alunite, which according to the thermodynamic data (LOPEZ AGUAYO et al., 1977), precipitates in a rather acid medium, at pH somewhat lower than 4 in the presence of kaolinite and an excess of silica, would already appears at the moment of the mixture, as may be seen from, fig. 2.

The observation of the proceding micrographs shows that opal-CT only appears in the form of blades and spherical aggregates when its growth is not inhibited: compare fig. 3 with those which evidence the existence of holes, figs. 10-13. This underline the importance of the porosity of the material and of the surface phenomena.

The solubility of silica is classically considered to be constants in the pH range 2-8.5. Amorphous silica is more soluble than the crystaline polymorphs; the solubility of these latter increases parallel to the increase in the degree of their disorder (FOURNIER, 1973). On the other hand, the data reported by SOSMAN (1965) shows that the density of silica gel is much less than the disordered silica polymorphs cristobalite-trydimite; the transit of the amorphous variety to the crystaline ones, therefore, implies a decrease in volume.

The use of oxygen isotopes (MURATA et al., 1977) has made possible to show that the change from amorphous silica to disordered cristobalite must imply a solution which is followed by a deposition. Within the cristobalite, however, the change from disordered forms to more ordered ones, measured by a descrease in the d(001) spacing, seems to correspond to a zero-order reaction (in solid state), with no solution being required.

Thus, the dispositions observed in the micrographs are explained by a deposition of opal-CT from solutions of amorphous silica, implying a decrease in volume and a possible creation of gaps in the places where the said mineral appears. The structural reorganizations in solid state (an increase in ordered forms) imply a parallel appearance of more empty spaces: note the morphological heterogeneity of the crystals and holes in figs. 7, 6, 9, 11, etc.

ILER (1955) reports that the silica surfaces are covered with a layer of hydroxyl ions, chemically bonded to the silicium atoms, and, therefore, there are negatively charged particles (silanol groups); a strong H^+ concentración can annul this charge, in the case of silica with a pH less than 2. If this situation does not arise (remember that in this case the association alunite-opal CT-kaolinite and/or other, several, have a pH around 4), the surface silanol groups could react with cations to forms complexes; the thermodynamic calculation of DUGGER et al. (1964) imply that every positive ion which is hydrolyzed at certain pH forms complexes with the silanol groups of similar stability. That is to say that at pH of more than 2, reasonable for geological media, it is probable that the presence of some ions will occurs: the existence, precisely, of elements which generate cations, with easy hydrolysis at acid or weakly acid pH. This has been corroborated in practice by detection in silica of noteworthy amounts of Al^{+3}, Fe^{+3}, Mg^{+3} and other, capable of forming silicated compound (HURD, 1973). This fact can explain the presence of alternative layers of opal-CT and silicates of metalic elements, fig. 7.

The presence of small spheres of silica in opals was demostrated in the laboratory (JONES et al., 1966). These authors attaked biotite with strong acid and noted the appearence of rounded masses of silica. ILER (1965) and op. cit.) had already reported that the precipitation of silica from aqueous solutions was begun by spheres. If, as is normal, metallic ions were present in the solution, the electric charge of the said spheres (which spould impede their regrouping by repulsion is neutralized by the formation of silicated complexes and these spheres, of reduced size, may also accumulate by flushing out in a liquid medium.

In this case, it can nobe said that there existed an important cluster of these espheres; of course, the ILER (ops. cit.) observation with respect to siliceous is likely. With the increase in diameter of the spheres, without any evidence that they are displayed, it is necessary to point out that the normal repulsion (negatively charged surfaces) is less than its overlapping, conditions which may arise in crystalization situations particulary free and contain no cations impurities which might stop the process in its early stages, such as may be seen in figs. 10, 11 and

13. In some cases were ions in sufficient quantities to interrup the process of the mechanism, a fact manifested by the presence of later autormorphic minerals, in the gaps, fig. 15.

CONCLUSION

The silifications in the Prelutetien continental sediments of Salamanca show morphological features similar to those reported for opals from other parts of the world, and they are interpreted as weathering products, generated by precipitation and later evolution (diagenesis) of silica from supersaturated solutions; the presence of other ions conditions the morphology of the silica polymorphs.

ACKNOWLEDGMENT

The authors are greateful to Mistress Millán for their practical assistence at laboratory and for useful discussions.

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Fig. 1.—Kaolinite crystals (in packets of leaves) coverld by opal. Carrascalino, 2.500 x.

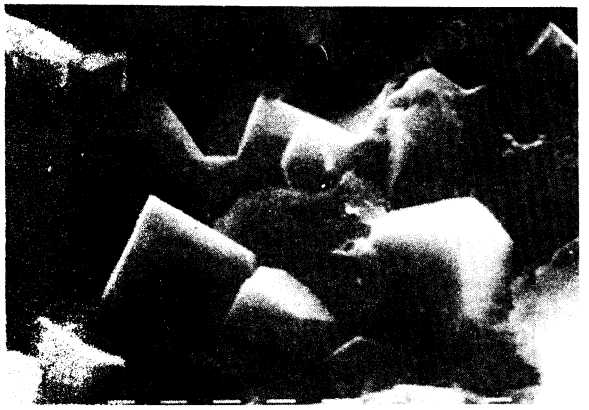

Fig. 2.—Dispersed alunite crystals in an opaline mass. The holes correspond to crystals, which have disappeard, from this mineral. Salamanca, 5.000 x, scale length 1 μm.

Fig. 3.—Compact nodules of opal. Aldearodrigo, 2.500 x.

Fig. 4.—Enlargement of part of fig. 3, 5.000 x.

Fig. 5.—Enlargement of part of fig. 3, 5.000 x.

Fig. 6.—Subparallel opal-CT blades. Aldearodrigo, 5.000 x.

Fig. 7.—Opal-CT layer alternating with other constituted for Fe minerals. Carrascalino, 1.250 x.

Fig. 8.—Opal-CT blades schowing dispositions of the individual crystals from different orientations. Carrascalino, 20.000 x.

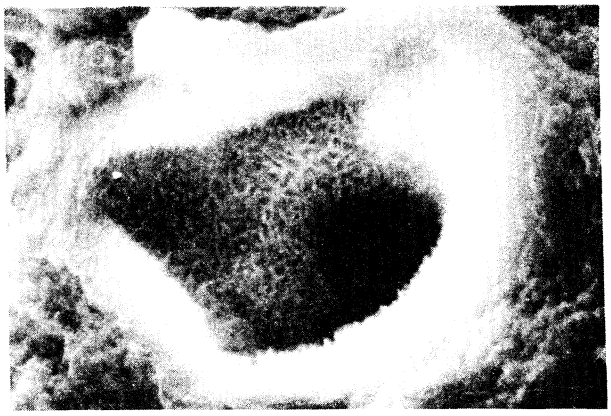

Fig. 9.—Opal-CT crystallites coating interior of wall of a hole. Aldearodrigo, 5.000 x, scale lengt 1 μm.

10.—Spherical aggregates of thin platelets of opal-CT. Carrascalino, 10.000 x, scale length 1 μm.

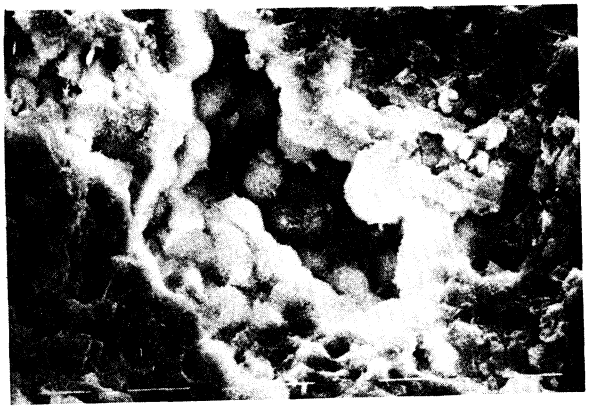

Fig. 11.—Opal-CT lepispheres in a cavity in the compact nodules opaline mass (fig. 3). Aldearodrigo, 1.250 x, scale length 10 μm.

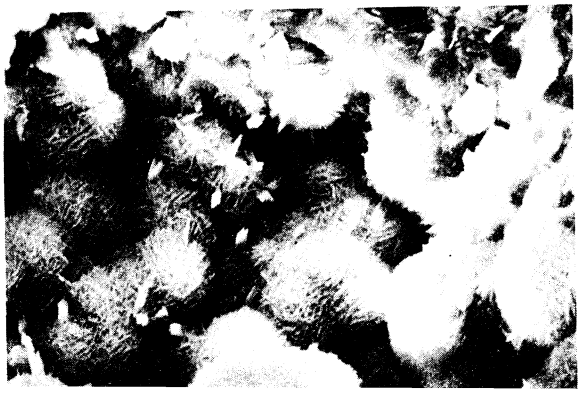

Fig. 12.—Aggregates of lepispheres. Aldearodrigo, 2.500 x.

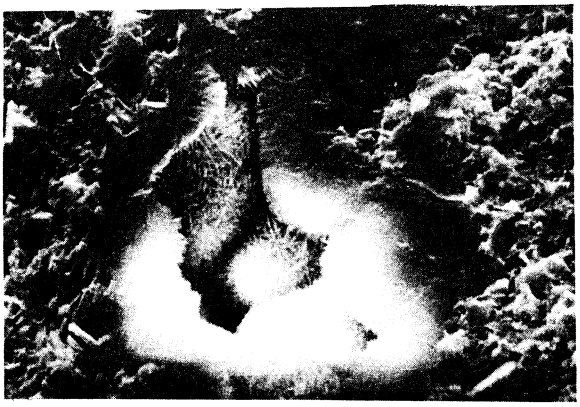

Fig. 13.—Lephispheres of opal-CT in a cavity in the silica mass, which enveloping kaolinite crystals. Carrascalino, 2.500 x.

Fig. 14.—Enlargement of part of fig. 11. Iron minerals on Opal-CT, 10.000 x, scale length 1 μm.

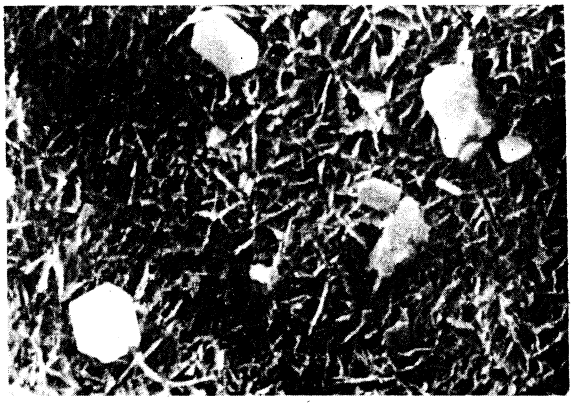

Fig. 15.—Crystals of other minerals appear on opal-CT. Aldearrodrigo, 10.000 x.